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Letter to the Editor

Mean atomic volume and T_g of Cu–Ge–As–Se glasses

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Abstract

Results of measurements of the mean atomic volume (V), the glass transition temperature (T_g) and the activation energy for glass transition (E_t) are reported for 11 glass compositions of the Cu–Ge–As–Se system. The compositions studied can be represented as $Cu_x(Ge_{0.125}As_{0.25}Se_{0.625})_{100-x}$ glasses. In the V–x, T_g–x and the E_t–x data of these glasses, changes in slope are observed at an x value of ~2. The results are consistent with a picture wherein, up to ~2 atomic percent (at.%), Cu atoms occupy interlayer positions between the uncorrelated layers of the parent glass matrix without affecting either the medium or the short range ordering of the parent glass. The results also suggest that up to ~2 at.%, Cu atoms act as 'plasticisers' in the parent glass matrix, reducing its T_g.

The role of metallic additives, namely, of Ag and Cu in modifying the mean atomic volume (V), the glass transition temperature (T_g) and electrical conductivity (σ) of the As_2Te_3 and the $[0.5As_2Se_3–0.5As_2Te_3]$ glasses were reported in our earlier communications [1–6]. Changes in slope in the property–composition data were observed at the composition with ~2 to 3 at.% of the metallic additive. Analysis of the data indicated [1–6] that small amounts of the metallic additive do not affect the short range or the medium range ordering of the parent (host) glass and therefore do not drastically alter the structure of the parent glass. For higher concentrations of the additive (generally greater than ~2 to 3 at.%), formation of bonds between the metallic atoms and the elements of the parent glass were indicated. The observed property dependence was rationalised by considering the formation of structural units (s.u.) of the metal with the elements of the parent glass. The studies also indicated [1–6] the necessity of generating the corresponding E_t-composition data for inferring the true T_g-composition dependencies in many systems.

In order to study some Ge-based chalcogenide glass systems, we tried to synthesise the $GeSe_2$ glass with Cu and Ag as additives, but were unsuccessful in synthesising these glasses. We were, however, successful in synthesising the $[0.5GeSe_2–0.5As_2Se_3]$ glass with an addition of up to 10 at.% of Cu by using the two-stage quenching method [1,3,4,7]. In this communication, the results of measurements of the V and T_g of the parent glass $[0.5GeSe_2–0.5As_2Se_3]$ and of 10 glass compositions, with Cu ranging from 0.3 to 10 at.%, are reported. The compositions of the glasses are hereafter referred to in terms of the at.% proportions of the elements. Accordingly, with the parent glass $[0.5GeSe_2–0.5As_2Se_3]$ denoted as $Ge_{12.5}As_{25}Se_{62.5}$, the glasses studied (Table 1) can

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Table 1
Data of density, V, T_g and E_t (kcal mol^{-1}) of the $Cu_x(Ge_{0.125}As_{0.25}Se_{0.625})_{100-x}$ glasses

x	d (g cm^{-3})	V (cm^3)	V (cal) (cm^3)	E_t	T_g in K at various heating rates (K min^{-1})				
					2.5	5	10	20	40
0	4.447 ± 0.005	17.35	17.350	83.7	488.0	491.5	495.5	499.3	503.7
0.3	4.456 ± 0.002	17.30	17.298	77.7	480.5	484.7	488.8	492.6	497.5
0.6	4.467 ± 0.002	17.25	17.246	70.8	478.0	482.7	486.7	491.2	496.7
1.0	4.483 ± 0.004	17.18	17.177	69.0	477.7	482.2	486.5	490.8	596.0
2.0	4.514 ± 0.005	17.03	17.003	68.0	477.5	482.2	486.0	490.6	495.8
2.5	4.534 ± 0.004	16.94	–	68.0	477.5	482.3	486.5	491.2	496.0
3.5	4.562 ± 0.006	16.81	–	70.7	477.9	482.5	486.7	491.0	496.1
5.0	4.607 ± 0.004	16.60	–	73.0	479.2	482.7	486.7	491.9	496.2
6.5	4.656 ± 0.002	16.38	–	74.6	479.8	483.3	487.2	493.0	496.6
8.0	4.698 ± 0.002	16.19	–	76.0	480.6	483.9	487.6	493.4	497.3
10.0	4.761 ± 0.003	15.92	–	77.0	480.9	484.3	489.2	493.4	497.2

be represented as $Cu_x(Ge_{0.125}As_{0.25}Se_{0.625})_{100-x}$, with each glass being specified in terms of x, its Cu content in at.%.

The details of the synthesis of the glasses, the methods and the set up adopted for measuring the density and T_g, the evaluation of the activation energy E_t of glass transition [from the slope of the linear $\log(T_g^2/\alpha)$ vs. $1/T_g$ data], along with the precautions necessary are all already described in detail elsewhere [1,3,4,6,8]; only the results are presented here.

Figs. 1–3 and Table 1 summarise the data of the present study. In the V–x data (Fig. 1), a change in slope is observed at $x \sim 2$; this slope change is clearer in the inset of the Fig. 1 in which the range of x has been restricted. In the T_g–x data (Fig. 2) of these glasses, an initial decrease of T_g with x, for x values up to ~2 is followed by a marginal increase of T_g with x for $x > 2$. Fig. 3(a) is a plot of $\log(T_g^2/\alpha)$ vs. $1/T_g$ data for three compositions with $x = 0$, 0.3, and 0.6. The data points for other compositions lie in the region between the data for $x = 0.3$ and $x = 0.6$, and have therefore not been depicted in Fig. 3. The E_t–x data of these glasses estimated from the slope of the $\log(T_g^2/\alpha)$ versus $1/T_g$ data are depicted in Fig. 3(b). E_t also initially decreases for x values up to ~2, and then shows an increase for higher values of x. The initial decreases of T_g and E_t with x are larger for x between 0 to 1 and the decrease is less steep for x between 1 and 2.

The results are discussed by adopting: (i) the general picture already used for understanding the properties of $As_{40}Te_{60}$ and $As_{40}Se_{30}Te_{30}$ glasses on introduction of Ag and Cu [1–6]; (ii) the gross general structure of chalcogenide glasses [9–14]; chalcogenide glasses have a corrugated layer

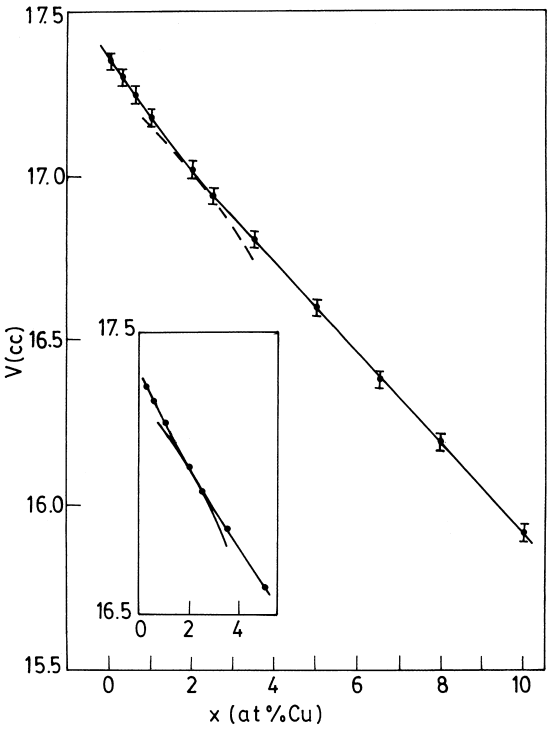

Fig. 1. V–x data for the $Cu_x(Ge_{0.125}As_{0.25}Se_{0.625})_{100-x}$ glasses. The change in slope at $x \sim 2$ is rendered clearer in the inset. The lines are drawn as a guide to the eye.

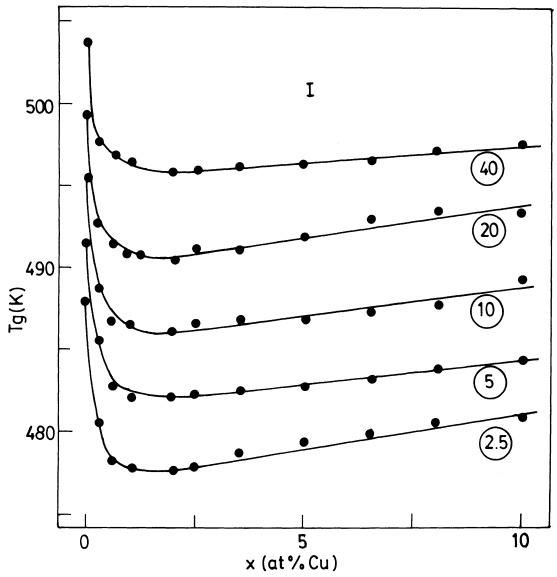

Fig. 2. T_g–x data for the $Cu_x(Ge_{0.125}As_{0.25}Se_{0.625})_{100-x}$ glasses at various heating rates from 2.5 to 40 K min^{-1}. The curves through the data points are drawn as guide to the eye.

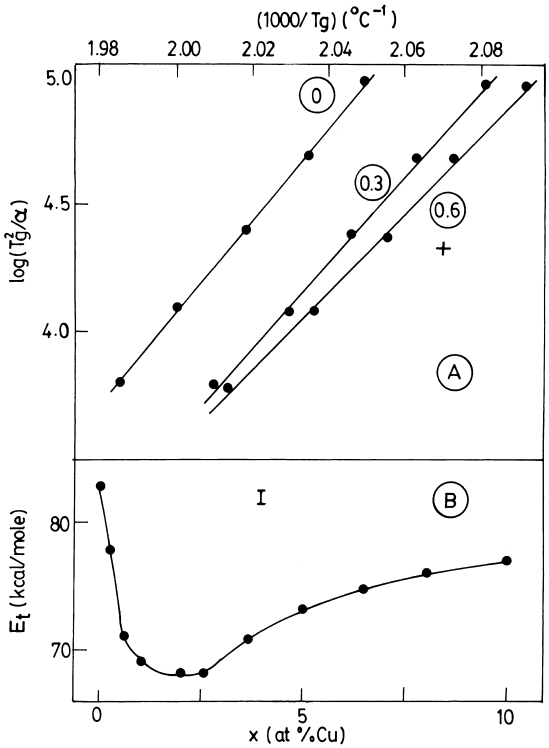

Fig. 3. (a) $\log(T_g^2/\alpha)$ vs. $(1/T_g)$ data for compositions with $x = 0$, 0.3 and 0.6. The data for the other compositions lie between the data of $x = 0.3$ and $x = 0.6$ and are not included in the figure to avoid confusion. (b) E_t–x data for the $Cu_x(Ge_{0.125}As_{0.25}Se_{0.625})_{100-x}$ glasses.

structure with finite layer thickness. The short range ordering in these materials corresponds to the formation of the respective structural units and their interconnection. The interconnection extends along a layer, the interlayer separation being typically ~0.4 to 0.5 nm. The medium range ordering (also called the intermediate range ordering) in these glasses extends to generally about four correlated layers, i.e. ~1.6 to 1.8 nm [9–14].

A cursory examination of the V–x, and T_g–x data obtained presently indicates that these results are qualitatively similar to those observed [1,3,4,6] upon introduction of Cu and Ag to the $As_{40}Te_{60}$ and the $As_{40}Se_{30}Te_{30}$ glasses; the data [1,3,4,6] of $Ag_x(As_{0.4}Te_{0.6})_{100-x}$, $Cu_x(As_{0.4}Te_{0.6})_{100-x}$, $Cu_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ and the $Ag_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses have been reproduced in the Figs. 4 and 5 for purposes of ready reference. In these systems (Figs. 4 and 5), changes in slope are observed in the V–x and T_g–x data at x values between 1 to 3 for the various systems. The following conclusions were arrived at [1–6] from these studies. (i) In small concentrations, generally from ~1 to 3 at.%, the metal atoms do not drastically affect the basic structure of the parent glass. (ii) Assuming a uniform distribution of the metal in the matrix of the parent glass, the distance between the clusters of metallic atoms turns out to be greater than that of the range for medium range ordering, (which is typically ~1.6 to 1.8 nm for chalcogenide glasses) for x from ~1 to 3 at.%. (iii) For higher concentrations, the metallic atoms affect the medium and short range ordering of the parent glass by forming bonds with the elements of the parent glass. (iv) The properties of the resulting glasses can be rationalised by considering the formation of various structural units of the metal with the elements of the parent glass (e.g. formation of Ag_2Te structural units in the As–Ag–Te system, of the Cu_2Te structural units in the As–Cu–Te system, of the $CuAsSe_2$ and the CuAsTe structural units in the As–Cu–Se–Te system, and the Ag_2Te and

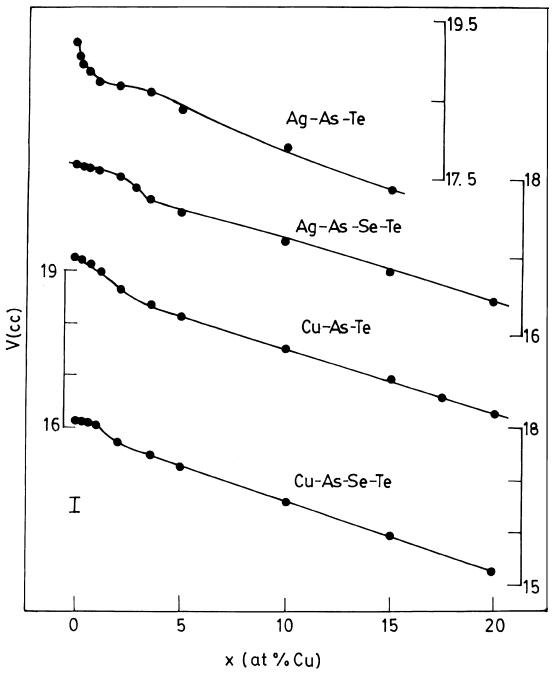

Fig. 4. V–x data [1,3,4,6] for the $Ag_x(As_{0.4}Te_{0.6})_{100-x}$, $Cu_x(As_{0.4}Te_{0.6})_{100-x}$, $Cu_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ and the $Ag_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses.

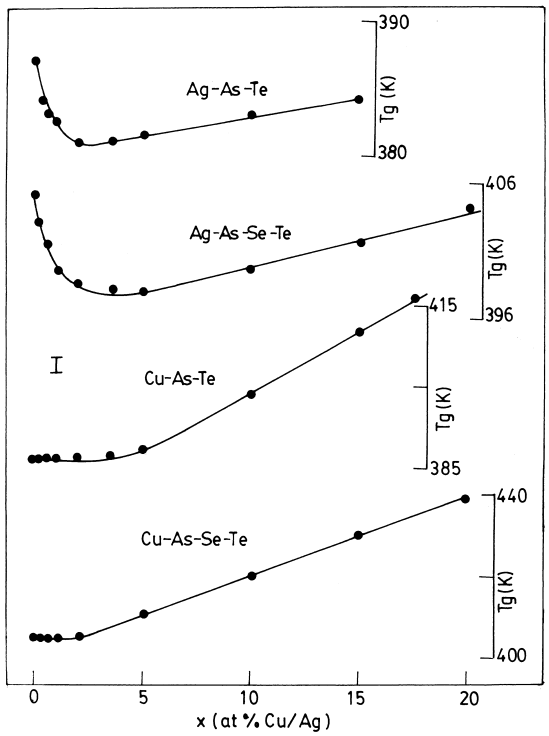

Fig. 5. T_g–x data [1,3,4,6] for the $Ag_x(As_{0.4}Te_{0.6})_{100-x}$, $Cu_x(As_{0.4}Te_{0.6})_{100-x}$, $Cu_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ and the $Ag_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses.

Ag_3AsSe_3 structural units in the As–Ag–Se–Te system).

Based on these general conclusions [1–6], it can be concluded that in the Cu–Ge–As–Se glasses studied presently also, the Cu atoms up to ~2 at.% do not alter the basic structure of the parent glass as they lie outside the purview of medium range ordering. In the $Cu_x(As_{0.4}Te_{0.6})_{100-x}$ and $Cu_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses it is found that Cu atoms, for concentrations less than ~3 at.%, occupy interlayer positions between the uncorrelated layers in the layered network of the parent glass [3,4]. If a similar picture is assumed for Cu in the $Ge_{12.5}As_{25}Se_{62.5}$ glasses also, then the Cu atoms, per se, do not contribute to the total V because of their interlayer occupancy; the resulting V of the $Cu_x(Ge_{0.125}As_{0.25}Se_{0.625})_{100-x}$ glasses (for addition of Cu up to 2 at.%) is evaluated as $V = mV_{Ge_{12.5}As_{25}Se_{62.5}}$, where m is the mole fraction of $Ge_{12.5}As_{25}Se_{62.5}$ in that composition. The V values thus calculated [V(cal)], using a value of 17.35 cm^{-3} for the V of $Ge_{12.5}As_{25}Se_{62.5}$ glass, are in good agreement with the experimental data (Table 1). Data on $Ag_x(As_{0.4}S_{0.6})_{100-x}$ glasses [15], which show a change in slope at an x value of 0.4 at.% in the E_t–x, elastic modulus C_{44}–x, and the intensity of excess light scattering versus x data, are of interest in this connection; this result has been interpreted [15] in terms of the modulation of the interlayer correlation, according to which Ag > 0.4 at.%, disturbs the interlayer correlation ranging over four layers in the host As_2S_3 matrix.

If clusters of Cu atoms, up to x ~2, are occupying interlayer positions (without affecting the short range or the medium range ordering of the parent glass), then it can be expected that the T_g of the $Cu_x(Ge_{0.125}As_{0.25}Se_{0.625})_{100-x}$ glasses are invariant with x for x from 0 to ~2, as the interlayer attractive and repulsive forces are not altered for x up to 2. In the systems depicted in Fig. 5 also, T_g is expected to be invariant with x for x values up to ~2. T_g is indeed found to be invariant with x

(Fig. 5) for x from $\sim$1 to 3, in the case of Cu–As–Te and the Cu–As–Se–Te systems [3,4]. In the Ag–As–Te and the Ag–As–Se–Te systems however, a decrease of T_g with x is observed (Fig. 5) for x values up to $\sim$2; but a closer examination of the data indicated [1,6] that the observed decrease of T_g was only apparent and it is a manifestation of the steep increase of the E_t of these glasses with x over the same range of x. If this is taken note of, then it is found that the T_g in the Ag–As–Te and the Ag–As–Se–Te systems are indeed invariant with x, for x up to $\sim$2.

The T_g–x and the corresponding E_t–x data in the Cu–Ge–As–Se system studied presently, are interesting in that they are different from the data of the Ag–As–Te and Ag–As–Se–Te systems discussed above. In the Cu–Ge–As–Se system, both T_g (Fig. 2) and E_t (Fig. 3(b)) decrease for x up to $\sim$2, unlike that observed in the Ag–As–Te and Ag–As–Se–Te systems. The decrease of T_g with x (for x up to $\sim$2) observed presently in the $Cu_x(Ge_{0.125}As_{0.25}Se_{0.625})$ glasses is, therefore, a true effect and not an artefact of the E_t–x dependence as observed [1,6] in the Ag–As–Te and Ag–As–Se–Te glasses. While the change in slope in the V–x data occurs at $x \sim 2$ (Fig. 1), the reduction in T_g with x is larger for x between 0 and 1 compared to that between 1 and 2 (Fig. 2).

The observed decrease of T_g with x (Fig. 2) indicates that the parent glass is 'softened' as Cu is added to the host $0.5GeSe_2$–$0.5As_2Se_3$ network. The reason for this behaviour is not very clear at present. However, results obtained for the $[GeS_2$–$Ag_2S]$ and $[GeS_2$–Ag_2S–AgI] glasses [16,17] are of relevance in the present context. A decrease of T_g of the $[GeS_2$–$Ag_2S]$ glasses is observed on addition of AgI; structural studies of the $[GeS_2$–Ag_2S–AgI] glasses indicate [17] that there is a distortion of the GeS_2 tetrahedra and a decrease of its cluster size on addition of AgI, even though Ge–I bonds are not formed. The AgI does not enter into the molecular clusters [17] but remains outside; AgI thus acts as a 'plasticiser' facilitating cooperative cluster movements. The results obtained presently are akin to these results. It can therefore be conjectured that in the Cu–Ge–As–Se glasses also, clusters of Cu atoms (up to $\sim$2 at.%) result in distorting the $GeSe_2$ tetrahedra of the parent glass and facilitate cluster movements, thereby acting as a plasticiser, leading to softening of the parent matrix and thus reducing its T_g. However, further work is needed to support this conclusion. Also of interest in the context of the results obtained presently are the data [18] on $[As_2S_3$–CuI] glasses. Structural studies on these glasses have indicated [18] that addition of CuI to As_2S_3 glass does not alter the maximum position of the First Sharp Diffraction Peak (which is determined by some repetitive characteristic distance between the structural units) but alters only its width (which is related to the correlation length, which represents the scale of the medium range ordering). It is concluded [18] that there are no strong interactions between the As_2S_3 and CuI structural units but the disturbance caused by the CuI molecules located between the layers of the As_2S_3 network that introduce additional disorder and have effects on the correlation length.

For Cu > 2 at.%, medium range correlation gets modified, with the Cu atoms affecting the short and medium range ordering of the parent glass by forming bonds with the elements of the parent glass. Apart from the well-known ternary compound $CuAsSe_2$, formation of several binary compounds of Cu with As (such as Cu_3As, Cu_5As_2) and with Se (such as Cu_2Se, CuSe, Cu_3Se_2) are indicated in the literature [19]. An examination of the results necessitates knowledge as to which of these structural units are formed in the various compositions of the Cu–Ge–As–Se system. Structural studies on Cu–Ge–As–Se glasses are not yet available for examining these results.

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References

[1] S. Mahadevan, A. Giridhar, J. Non-Cryst. Solids 197 (1996) 219.

[2] A. Giridhar, S. Mahadevan, J. Non-Cryst. Solids 197 (1996) 228.
[3] S. Mahadevan, A. Giridhar, J. Non-Cryst. Solids 221 (1997) 281.
[4] A. Giridhar, S. Mahadevan, J. Non-Cryst. Solids 238 (1998) 225.
[5] A. Giridhar, S. Mahadevan, J. Mater. Sci. 34 (1999) 1281.
[6] S. Mahadevan, A. Giridhar, J. Non-Cryst. Solids 258 (1999) 207.
[7] A. Hruby, L. Stourac, Mater. Res. Bull. 6 (1971) 465.
[8] S. Mahadevan, A. Giridhar, J. Non-Cryst. Solids 134 (1991) 94.
[9] L.E. Busse, Phys. Rev. B 29 (1984) 3639.
[10] K. Tanaka, Phys. Rev. B 39 (1989) 1270.
[11] A.C. Wright, R.A. Hulme, D.I. Grimley, R.N. Sinclair, S.W. Martin, D.L. Price, F.L. Galeener, J. Non-Cryst. Solids 129 (1991) 213.
[12] A.A. Vaipolin, E.A. Porai Koshits, Sov. Phys. Solid State 5 (1963) 186.
[13] P.P. Seregin, L.N. Vasilev, Sov. Phys. Solid State 13 (1972) 2258.
[14] J.R. Fitzpatrick, C. Maghrabi, Phys. Chem. Glasses 12 (1971) 105.
[15] K. Matsuishi, H. Kasamura, S. Onari, T. Arai, J. Non-Cryst. Solids 114 (1989) 46.
[16] E. Robinel, B. Carette, M. Ribes, J. Non-Cryst. Solids 57 (1983) 49.
[17] A. Ibanez, E. Philippet, S. Benazeth, H. Dexpert, J. Non-Cryst. Solids 127 (1991) 25.
[18] S. Mamedov, A. Bolotov, L. Brinker, A. Kisliuk, M. Soltwisch, J. Non-Cryst. Solids 224 (1998) 89.
[19] J.A. Dean, Langes Handbook of Chemistry, 12th Ed., McGraw Hill, New York, 1979.